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In situ tritium production and fluid mean residence times in the two subsystems of the Valles Caldera hydrothermal system, New Mexico

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IN SITU TRITIUM PRODUCTION AND FLUID MEAN RESIDENCE TIMES IN THE TWO SUBSYSTEMS OF THE VALLES CALDERA HYDROTHERMAL SYSTEM, NEW MEXICO

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Abstract—Tritium (^{3}H) concentrations in precipitation are used to calculate fluid mean residence times using two end-member cases, piston-flow and well-mixed reservoirs. These simplified models using ^{3}H yield relative fluid mean residence times in different portions of the system. In situ ^{3}H production in the reservoir through neutron interaction with ^{6}Li is considered, and only very low levels of ^{3}H (0.01 T.U.) contribute to the waters by this process. Calculations using the end-member cases at Valles caldera indicate that mean residence times of geothermal waters in the reservoir are between 3000 and 10,000 yrs, if all post-bomb ^{3}H has entered and mixed with the reservoir waters. The results from this model indicate that the two distinct subsystems of the main reservoir are associated with different fluid mean residence times. Waters in the Redondo Creek subsystem are older (4300 to >10,000 yrs) than waters in the Sulphur Springs subsystem (2000 to 4400 yrs). When accounting for the likelihood that not all post-bomb recharge water has mixed with the reservoir fluids, much younger mean residence times are obtained (660 to 1280 yrs). The oldest water occurs in the Redondo Creek subsystem, but some waters in this subsystem are similar in age to those at Sulphur Springs, possibly suggesting stratification in the reservoir. Comparison of the results of the end-member cases with those obtained using more sophisticated methods indicates that the two end-member cases, with the use of ^{3}H, can provide acceptable limits (order of magnitude) on a fluid's mean residence time and volumes within a reservoir.

INTRODUCTION

Because tritium (^{3}H) has a half-life of 12.43 yrs, and generally behaves conservatively, the ^{3}H content of waters is a reliable indicator of mixing and relative groundwater ages. Numerous studies of surface and groundwater ages (or residence times) and mixing rates have been conducted over the years with the use of ^{3}H (e.g., Begemann and Libby, 1957; Eriksson, 1958; Nir, 1964; Carmi and Gat, 1973; Simpson and Carmi, 1983; Vuataz and Goff, 1986). Discussions of well-mixed versus piston-flow behavior have been abundant in these and other studies, with several different methods of treating the cases being presented.

The ^{3}H computer model used in this paper (derivation and the Fortran code described by Shevenell, 1991; Shevenell and Goff, 1995) involves a procedure that places limits on groundwater mean residence times and reservoir volumes by calculating two end-member cases utilizing known ^{3}H input into the system. The end-members are the piston-flow model, which requires that no mixing occur in the reservoir, and the well-mixed model, which assumes that the reservoir fluid is completely mixed with all fluids that enter the system. The two end-member cases provide upper and lower limits on mean residence times of fluids in a system, which can be useful information when comparing different waters, or when studying a system in which the hydrologic characteristics are poorly known (e.g., Mount St. Helens; Shevenell, 1991).

Based on geochemical data, the geothermal fluids in Valles caldera originate from two distinct subsystems within the caldera (Goff et al., 1992; Goff and Gardner, 1994). Although the high temperature waters from both subsystems have similar ^{3}H contents (all < 1 T.U.), modeling of mean residence times of the waters yields different results because samples were collected in different years and ^{3}H contents in precipitation have varied markedly year to year since 1953. The current work uses ^{3}H to estimate fluid mean residence times of Valles caldera geothermal reservoir waters. The purpose of this work is to estimate fluid mean residence times in the two subsystems within the caldera.

GEOLOGY AND HYDROGEOLOGY OF THE VALLES CALDERA

The Jemez volcanic field is located at the intersection of the northeast-trending Jemez lineament and the Rio Grande rift (Mayo, 1958; Laughlin et al., 1976). The geology of the Jemez Mountains consists of about 2000 km^3 of Tertiary to Quaternary volcanic rocks that overlie Tertiary basin-fill sedimentary rocks within the rift, and Paleozoic and Mesozoic sedimentary rocks and Precambrian basement west of the rift margin. During the 1960s and 1970s, Union Oil Company of California drilled 24 deep geothermal wells within Valles caldera (Union, 1978; 1982; see Fig. 1) to evaluate the geothermal potential of the area. Numerous studies on the geology, structure and geothermal hydrology of the region have been conducted using data from these wells and from Continental Scientific Drilling Program coreholes (i.e., Goff and Gardner, 1988; Goff et al., 1989; Goff and Gardner, 1994). The geothermal reservoir within the Valles caldera largely resides in caldera-fill tuffs and tuffaceous sediments and locally extends into underlying pre-caldera volcanics and basin sediments of the Rio Grande rift.

Recharge to the geothermal system occurs within the northeast portion of the caldera depression and highlands surrounding the caldera (Vuataz and Goff, 1986), and possibly along the ring fracture faults (Faust et al., 1984). Meteoric waters circulate deeply within the caldera and are heated to temperatures of up to 300°C. Two up-flow zones representing two geochemically distinct subsystems of the reservoir have been identified within the caldera: the Sulphur Springs subsystem, near the western margin of the resurgent dome (at VC-2A on Fig. 1); and the Redondo Creek subsystem within a keystone graben of the resurgent dome (at Baca 4, 13, 15, 19 on Fig. 1). The two subsystems are fault-controlled reservoirs separated from each other by 2 to 3 km of lower permeability,

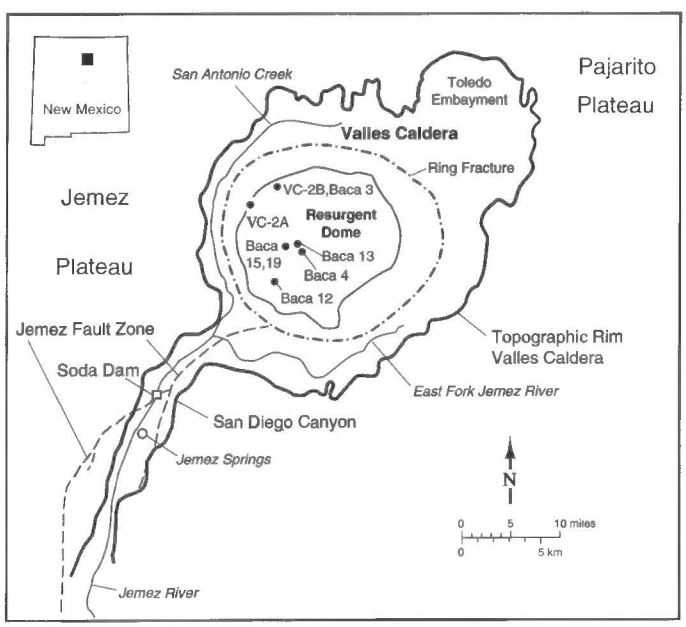


FIGURE 1. Geothermal water sampling locations in and near Valles caldera, New Mexico.

hydrothermally altered, caldera-fill rocks. Geochemically, Sulphur Springs fluids are more concentrated in dissolved solids, particularly in B and Cl, and heavier in $\delta^{18}O$ than Redondo Creek fluids. In addition, the He R/R_A ($^3He/^4He$ ratio in water to that in air) in the Sulphur Springs subsystem is slightly greater than that in the Redondo Creek subsystem, indicating a slightly larger mantle/magmatic component in the Sulphur Springs reservoir waters (Goff et al., 1992).

Researchers have estimated the average thickness of the Redondo Creek subsystem to be between 610 m (Bodvarsson et al., 1982) and 1830 m (Union, 1982) with porosities ranging from 3 to 5% (Faust et al., 1984; Bodvarsson et al., 1982). Discharge from the system is through a hydrothermal outflow plume where the flow is dominantly fault controlled, with only minor stratigraphically controlled flow. Up to 50% of the total discharge from the system is along the Jemez fault zone at Soda Dam and Jemez Springs (Fig. 1) where thermal fluids become mixed with young meteoric waters (Goff et al., 1988).

Several studies have been conducted that yield estimates on discharge rates from the system and volumes of fluid within the reservoir. The estimates indicate that the volume of fluid discharging from the system ranges from 5.07×10^{-4} km^3/yr to 1.77×10^{-3} km^3/yr, and the reservoir volume estimates range from 1.21 to 2.69 km^3 of fluid (Balleau, 1980; Bodvarsson et al., 1982; Union Oil, 1978, 1982; Faust et al., 1984). None of the estimates of reservoir extent or fluid volume distinguishes between the Sulphur Springs and Redondo Creek subsystems of the Valles geothermal system. Both Faust et al. (1984) and Bodvarsson et al. (1982) assumed relatively small lateral extents of the reservoir (31.08 and 40 km^2) and modeled only the "producible," hot region surrounding Redondo Creek. Union Oil also modeled the reservoir, yet they assumed that the reservoir resides within most of the 144 km^2 of the caldera.

METHODS

Procedure for estimation of in-situ tritium production

Tritium can be produced within a reservoir through the neutron-induced reaction:

$$^6Li(n, \alpha)^3H. \quad (1)$$

Because measured concentrations of ^3H in groundwaters at Valles caldera are quite low, in-situ production of ^3H by this reaction must be considered. The neutron production rate (neutrons/gm yr) due to spontaneous fission and (a,n) reactions is estimated using expressions presented in Andrews et al. (1989), which allow calculation of neutron flux as a function of total U and Th contents in the rock. The fraction (F) of these produced neutrons which encounter Li in the rock matrix is estimated by the following (Andrews and Kay, 1982):

$$F = \acute{o}_{Li} N_{Li} / \Sigma \acute{o}_i N_i \quad (2)$$

where $\acute{o}_{Li}$ = total neutron absorption cross-section; N_{Li} = Li abundance, $\acute{o}_i$ = total neutron absorption cross-section for all elements in the matrix; and N_i = abundance of all elements in the matrix. The factor F is multiplied by the neutron production rate to obtain the ^3H production rate in atoms/gm yr. One neutron will interact with one Li atom in the matrix to produce one ^3H atom. High concentrations of U, Th and Li could result in significant concentrations of ^3H being produced in the reservoir. However, high concentrations of B significantly reduce the number of neutrons interacting with Li because the adsorption cross-section of B (755 barns) is ten times larger than that for Li (71 barns; Andrews and Kay, 1982). Even low concentrations of Sm and Gd significantly reduce neutron interaction with Li as their adsorption cross-sections are 49,000 and 5820 barns, respectively. The ^3H content in pore waters resulting from neutron interaction with lithium is calculated from the ^3H production rate (P) by the equation (Andrews and Kay, 1982):

$$^3H\ (T.U.) = \frac{18 \times 10^{18}\ P}{\lambda \times \phi \times 2 \times 6.02 \times 10^{23}} \quad (3)$$

where λ (0.05576 yr^{-1}) is the ^3H decay constant, and ϕ is the total water content (structurally bound water and pore water). The other factors result because there are $2 \times 6.02 \times 10^{23}$ hydrogen atoms in one mole (18 g) of water, and one (3) atom in 10^{18} hydrogen atoms is the definition of 1 T.U.

Procedure for estimation of input tritium functions

Derivations of the piston-flow and well-mixed models appear in Shevenell and Goff (1995). In order to calculate end-member residence times, the ^3H concentration of recharged water before and after nuclear testing was estimated. Although there are very few ^3H data for years prior to 1952, a few measurements were made on lake waters, groundwaters, and wines from which an estimate of pre-bomb ^3H concentrations can be made. These measurements indicate that the average background ^3H value for the interior of North America is 6 T.U. (Kaufman and Libby, 1954; Craig and Lal, 1961), and this value was selected as the pre-1954 background ^3H concentration.

Precipitation data from Albuquerque, New Mexico (IAEA data) and from rain collectors near Valles caldera (Adams et al., 1995) are used to estimate input functions to the Valles caldera system. The Albuquerque station is missing data for the years 1953 to 1961, hence, these data are compared to the Ottawa, Canada station because this station has a complete record of ^3H in precipitation after 1953 (see Table 1; IAEA data).

TABLE 1. Tritium in precipitation for Albuquerque, New Mexico and Ottawa, Canada for the years 1952 to 1991.

Time	Albuquerque		Ottawa	
(year)	^3H (T.U.)	% of precip.	^3H (T.U.)	% of precip.
1952	6[a]	--	6[a]	--
1953	14.7[b]	--	26.4	43.0
1954	202.3[b]	--	287.7	92.3
1955	24.1[b]	--	41.3	100
1956	123.7[b]	--	183.8	100
1957	76.1[b]	--	118	100
1958	442.3[b]	--	587.2	100
1959	331.7[b]	--	451.6	100
1960	103.6[b]	--	156.3	100
1961	156.2[b]	--	227.3	100
1962	413.3	70.3	992.4	100
1963	1898.7	98.4	2900.1	100
1964	1688.3	99.5	1532.8	100
1965	484.1	96.6	778.2	100
1966	282.2	100	560.8	100
1967	237.6	97.1	324.2	100
1968	188.1	100	216.9	100
1969	193.6	100	253.7	55.8
1970	200.8	100	190.8	100
1971	163.8	100	206.1	86.6
1972	53.1	92.6	92.3	100
1973	71.0	100	90.4	100
1974	52.7	77.3	98.1	100
1975	50[c]	--	75.9	95.2
1976	63.4	90.9	58.9	100
1977	45.3	100	73.9	100
1978	46.9	100	73.6	99.8
1979	23.4	63.9	49.6	100
1980	23.3	100	49.5	100
1981	35.7	100	55.1	100
1982	28.9	100	39.7	100
1983	16.2	100	50.5	100
1984	15.1	100		
1985	19.7	100		
1986	17.3	100		
1987	12.2	--		
1990	11.8[d]	100		
1991	11.3[d]	100		

a assumed background values (see text)

b values calculated using known ^3H in Ottawa precipitation.

c calculated using linear relationship of ln(^3H) vs time at the Albuquerque station between 1972 and 1991.

d weighted mean ^3H concentration from 3 precipitation collectors near Valles caldera.

Note: All measured values are yearly weighted mean ^3H concentrations from data reported by the IAEA; "% of precip" is the amount of total yearly precipitation at a site which was available for calculating weighted mean ^3H concentrations.

The IAEA data at Ottawa have commonly been used to formulate ^3H input functions at other stations (e.g., Rabinowitz et al., 1977; Pearson and Truesdell, 1978; Campana and Mahin, 1985; Shevenell, 1991).

In order to estimate the missing ^3H data at the station between 1953 and 1961, the natural logarithms of ^3H at the two stations were compared, with the two being linearly correlated:

$$\ln(^3H_{ABQ} = 1.0967(\ln(^3H_{Ottawa})) - 0.8998, R^2 = 0.941 \quad (4)$$

The simple linear regression method estimates the missing ^3H data values quite well and the small standard deviation of ±3.76 T.U. is acceptable because the values being estimated lie between 14.7 and 442.3 T.U., and significant error could only be produced on one of the estimated values (in 1953, where the calculated value is 14.7 T.U., Table 1; Shevenell and Goff, 1995).

Tritium input functions

It is necessary to find a function that best describes the change in ^3H through time, and a linear least-squares regression was performed on each discrete line segment of Figure 2. Using the Albuquerque data to calculate input functions, a best-fit line between data points is constructed such that a yearly ^3H input function was obtained for the years 1953 to 1991 (see Fig. 2 for the 13 discrete line segments). The input functions ($C_{in}(t)$) for each period of years are described in and used with the well-mixed and piston flow model equations in Shevenell and Goff (1995). Thirteen terms for the 13 line segments represented by Figure 2 are added together and substituted into the appropriate equations in order to calculate the upper limit of mean residence times.

RESULTS

In-situ tritium production

Using expressions presented in Andrews et al. (1989) and equations (2) and (3), the ^3H produced in lithologic units within and near Valles caldera was estimated. Representative samples from each of the units listed in Table 2 were obtained from Gardner et al. (1986) and F. Goff (unpubl., 1995). Because the U, Th, Li, B, Sm and Gd contents of a rock are most important in determining the production of ^3H, several values for each of these parameters were used in different computations in order to obtain the maximum and minimum possible production in the rock. Two or three ^3H values were calculated for each unit. When measured Li and B were available for a sample, the minimum and maximum produced ^3H are reported. When no measured Li and B were available, the average crustal abundances were obtained for the particular lithology from Higgins (1988). Few of the samples had measured F or Gd, hence, an additional calculation is reported for ^3H using average crustal abundances noted in Hurlbut and Klein (1977). Perhaps the most realistic estimate of in situ ^3H production is obtained with the use of crustal Gd values given its large reaction cross-section, because at least a small amount is likely to be present in the rocks. For instance, for the Banco Bonito rhyolite sample, the maximum value calculated without Gd is 0.0092 T.U., whereas the addition of only 5.4 ppm Gd decreases the expected amount to 0.0077 T.U.

Because the average porosity value of the Bandelier Tuff (in which the majority of the fluids reside) is 3 to 5%, a value of 5% was used in the in-situ production calculations. Choice of this value necessarily influences the final results. Table 3 shows an example calculation under the assumption of different porosity values. As porosities are increased, the estimated ^3H content decreases. Only in the case of a porosity of 1% is any significant ^3H produced (i.e., 0.04 T.U.). These ^3H values are for liquid water and bound waters and it is unlikely that all produced ^3H atoms will diffuse from the matrix into fracture and intergranular porosity to be trapped by the fluids. Hence, these values are maxima. The expected in situ ^3H production from most units is very low, between 0.001 and 0.008 T.U. based on a porosity of 5%. Tritium production that approaches the analytical detection limit (0.01 T.U.) is only noted in one unit, the red beds of the Abo Formation. However, this value was calculated using a porosity of 5%, and it is likely that porosities are much higher in the sandstones and shales of this unit, and produced ^3H will be much lower in higher porosity rocks (e.g., Table 3). Clearly, the low values of in situ produced ^3H in all lithologies will not influence groundwater dating because the maximum possible produced values are too small and near the analytical ^3H detection limit.

Mean residence times

Figure 3 is a plot of the results of calculated ^3H concentrations versus mean residence times for the two end-member cases for waters collected in 1991. Expected ^3H contents associated with fluids of varying mean residence times for well-mixed and piston-flow reservoirs from samples collected for several years up to 1992, can be found in Shevenell and Goff (1995). The mean residence times derived from this work are applicable for fluids from aquifers of all types within the Four Corners region of the U.S.A. Figure 3 shows that non-unique mean residence times are obtained for ^3H contents greater than 10 T.U. This does not present a difficulty in interpreting the Valles caldera data. However, other study areas having younger waters and higher ^3H contents may suggest multiple residence times.

Fluids from geothermal wells in the Redondo Creek and Sulphur Springs reservoirs consistently have ^3H concentrations between 0.2 and 0.89 T.U. (±0.08 to 0.13 T.U.; Table 4) suggesting that reservoir fluids

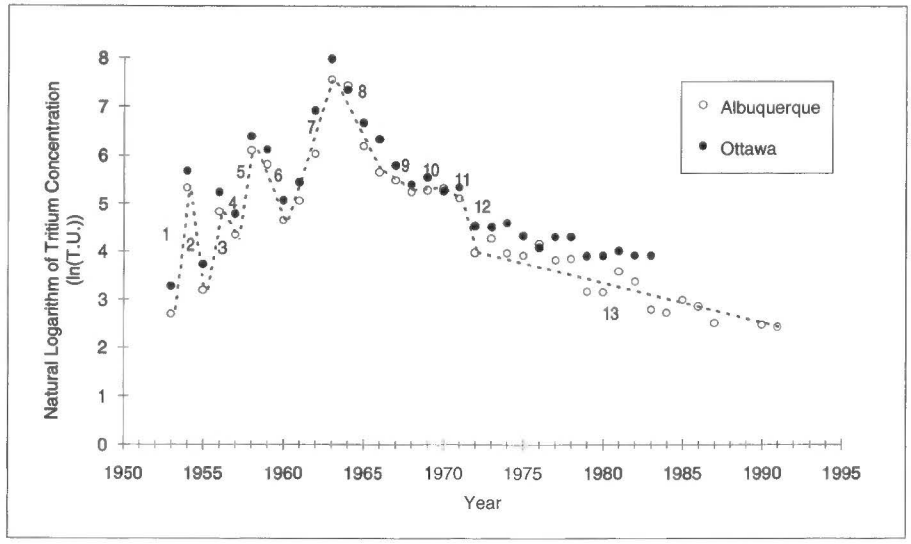


FIGURE 2. Distribution of the natural logarithm of tritium concentrations in precipitation at the Albuquerque, New Mexico and the Ottawa, Canada stations during the years 1953 through 1991. The numbers on the plot identify each of the 13 distinct line segments (see text).

TABLE 2. In-situ ^{3}H production for geologic units in Valles caldera, and the Pajarito Plateau.

			ppm								Tritium
Formation	Sample #	Ref	Li	B	Cl	F*	Sm	Gd	U	Th	(T.U.)
Banco Bonito	F82-7	Gard	30	13	500	0	4.5	0	5.7	23	0.0041
Banco Bonito	F82-7	Gard	68	9.9	500	0	4.5	0	5.7	23	0.0092
Ave Crustal F & Gd	F82-7	Gard	68	9.9	500	625	4.5	5.4	5.7	23	0.0077
Upper Band	F81-160	Goff	14	29	890	0	8.8	0	11	31	0.0026
Upper Band	F81-160	Goff	47	16	890	0	8.8	0	11	31	0.0092
Ave Crustal F & Gd	F81-160	Goff	47	16	890	625	8.8	5.4	11	31	0.0078
Tsankawi	F82-94	Goff	14	29	2200	0	16.6	0	11.8	40	0.0024
Tsankawi	F82-94	Goff	47	16	2200	0	16.6	0	11.8	40	0.0084
Ave Crustal F & Gd	F82-94	Goff	47	16	2200	625	16.6	5.4	11.8	40	0.0074
Tsankawi	F-82-95	Goff	14	29	1140	0	5.3	0	2.7	11	0.0009
Tsankawi	F-82-95	Goff	47	16	1140	0	5.3	0	2.7	11	0.0030
Ave Crustal F & Gd	F-82-95	Goff	47	16	1140	625	5.3	5.4	2.7	11	0.0026
Lower Bandelier	F83-45	Goff	14	29	340	0	9.2	0	8	22	0.0019
Lower Bandelier	F83-45	Goff	47	16	340	0	9.2	0	8	22	0.0070
Ave Crustal F & Gd	F83-45	Goff	47	16	340	625	9.2	5.4	8	22	0.0059
Guaje	F83-12	Goff	14	29	900	0	9.7	0	14	22	0.0023
Guaje	F83-12	Goff	47	16	900	0	9.7	0	14	22	0.0081
Ave Crustal F & Gd	F83-12	Goff	47	16	900	625	9.7	5.4	14	22	0.0069
Ign B	F82-92	Goff	10.5	21.75	1600	0	8	0	6.7	21.1	0.0012
Ign B	F82-92	Goff	35.25	12	1600	0	8	0	6.7	21.1	0.0042
Ave Crustal F & Gd	F82-92	Goff	35.25	12	1600	625	8	5.4	6.7	21.1	0.0036
Ign A	F82-91	Goff	10.5	21.75	1100	0	7.2	0	6.8	23	0.0013
Ign A	F82-91	Goff	35.25	12	1100	0	7.2	0	6.8	23	0.0045
Ave Crustal F & Gd	F82-91	Goff	35.25	12	1100	625	7.2	5.4	6.8	23	0.0038
Tschicoma Dacite	JG80-12	Gard	57	10.6	500	0	4.4	0	3.29	7.5	0.0035
Ave Crustal F & Gd	JG80-12	Gard	57	10.6	500	625	4.4	5.4	3.29	7.5	0.0030
Paliza Canyon And	JG80-28	Gard	57	10.6	0	0	5.8	0	2.62	7.7	0.0033
Ave Crustal F & Gd	JG80-28	Gard	57	10.6	0	625	5.8	5.4	2.62	7.7	0.0028
Paliza Canyon And	JG81-4B	Gard	57	10.6	620	0	6.1	0	2.92	9.4	0.0036
Ave Crustal F & Gd	JG81-4B	Gard	57	10.6	620	625	6.1	5.4	2.92	9.4	0.0031
Paliza Canyon Dacite	JG81-31	Gard	57	10.6	0	0	13	0	5.22	14.3	0.0065
Ave Crustal F & Gd	JG81-31	Gard	57	10.6	0	625	13	5.4	5.22	14.3	0.0054
Yeso	VC2B-3000	Goff	57	10.6	150	0	3.4	0	3.9	6.6	0.0040
Ave Crustal F & Gd	VC2B-3000	Goff	57	10.6	150	625	3.4	5.4	3.9	6.6	0.0032
Abo	VC2B3801	Goff	140	55	92	0	9.2	0	4.2	15.2	0.0079
Abo	VC2B3801	Goff	249	49.1	92	0	9.2	0	4.2	15.2	0.0133
Ave Crustal F & Gd	VC2B3801	Goff	249	49.1	92	625	9.2	5.4	4.2	15.2	0.0120
Madera	VC2B-4254	Goff	6	22.1	130	0.01	0.57	0	2.38	0.62	0.0001
Madera	VC2B-4254	Goff	176	0.7	130	0.01	0.57	0	2.38	0.62	0.0035
Ave Crustal F & Gd	VC2B-4254	Goff	176	0.7	130	625	0.57	5.4	2.38	0.62	0.0030
Sandia	VC2B-5052	Goff	88	22.6	46	0	1.62	0	2.34	1.05	0.0014
Sandia	VC2B-5052	Goff	168	18.7	46	0	1.62	0	2.34	1.05	0.0025
Ave Crustal F & Gd	VC2B-5052	Goff	168	18.7	46	625	1.62	5.4	2.34	1.05	0.0023
Qtz Monzonite	VC2B-5251	Goff	22	9.2	0	0	16.7	0	4.07	11.6	0.0017
Ave Crustal F & Gd	VC2B-5251	Goff	22	9.2	0	625	16.7	5.4	4.07	11.6	0.0015
Qtz Monzonite	VC2B-5350	Goff	22	9.2	0	0	12.7	0	4.07	8.3	0.0015
Ave Crustal F & Gd	VC2B-5350	Goff	22	9.2	0	625	12.7	5.4	4.07	8.3	0.0013
Qtz Monzonite	VC2B-5450	Goff	22	9.2	0	0	19.7	0	2.74	13.6	0.0015
Ave Crustal F & Gd	VC2B-5450	Goff	22	9.2	0	625	19.7	5.4	2.74	13.6	0.0013
Qtz Monzonite	VC2B-5700	Goff	22	9.2	0	0	14.6	0	4.38	8.7	0.0016
Ave Crustal F & Gd	VC2B-5700	Goff	22	9.2	0	625	14.6	5.4	4.38	8.7	0.0014

Note: Goff = Goff unpublished data; Gard = Gardner et al., 1986.
*Fluoride is reported in ppm, except for the numbers in bold which are in percent.
Average crustal abundances for F and Gd from Hurlbut and Klein, 1977 (page 123)
Li and B numbers in bold are average values from Higgins, 1988 for either sediments or volcanics.

are relatively well mixed and are quite old. If piston flow dominated in this fracture-controlled reservoir, ^{3}H contents would be expected to vary between sampling localities and sampling dates, but minimal variability is observed. Estimated piston flow ages of 40 to 70 yrs are, therefore, likely to substantially underestimate the residence times. Hence, the piston flow results are not considered further. Due to extensive flowing of these wells, we assume that there is no drilling fluid contamination.

The estimated mean residence times using the well-mixed model indicate differences in relative fluid ages between the two subsystems in Valles caldera. The fluids in the Redondo Creek area are generally older (4300 to >10,000 years) than those in the Sulphur Springs area (2000 to 4400 years), providing additional evidence that two distinct subsystems are present in Valles caldera.

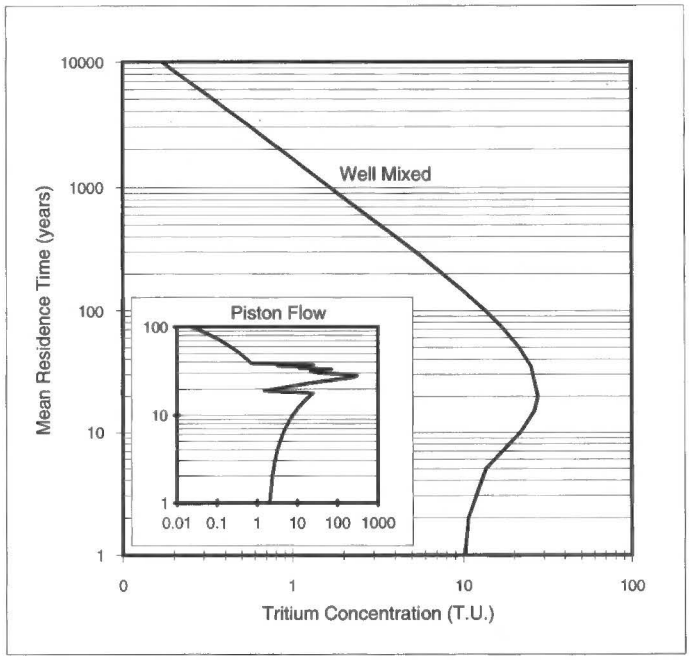


FIGURE 3. Results of the well-mixed and piston-flow models for the Albuquerque region for samples collected in 1991.

DISCUSSION

Very few, if any, systems can be described by pure piston-flow or pure well-mixed conditions. Clearly, piston flow ages are far too young for the deep reservoir waters in Valles caldera, and mean residence times must be greater than those indicated by this method. Although ^{3}H, with its short half life, cannot be used rigorously to obtain accurate ages of these old waters, this work shows that it can be used to obtain an order of magnitude estimate of fluid ages and help distinguish between different zones in a reservoir.

The results of the method applied here may be less accurate than more rigorous modeling efforts. For example, the current model does not explicitly investigate dispersive mixing along the flow path. Dispersion is instead conceptualized by assuming that the repeated, yearly recharge to a system, with variable ^{3}H, is introduced at numerous points in the reservoir such that previously recharged fluids in the reservoir will become completely mixed each year with every new influx of water. Deeper flow represented by streamlines at greater depths will, in reality, have different ^{3}H contents than shallower zones. In the well-mixed method, the assumption is made that these zones become mixed to form the concentrations measured in the field. This well-mixed assumption will not necessarily yield accurate fluid ages in the system, given the possibility of some amount of flow or chemical stratification in the reservoir. The current procedure tends to overestimate the amount of hydrodynamic dispersion occurring in a system, yet the objectives of the model are to estimate upper and lower limits on mean residence times of fluids in a reservoir. With this approach, information can be gained without prior knowledge of dispersion coefficients, reservoir volumes, or other aquifer parameters.

Estimated mean residence times of fluids assuming well-mixed conditions are likely too high because it is probable that some of the fluid

TABLE 3. Example calculations of in situ tritium production in the upper Bandelier Tuff for different assumed porosity values.

	Porosity (in %)							
	1%	2%	3%	4%	5%	7.50%	10%	20%
Minimum values (no F or Gd)								
Tritium (T.U.)	0.0128	0.0064	0.0043	0.0032	0.0026	0.0017	0.0013	0.0006
Maximum values (no F or Gd)								
Tritium (T.U.)	0.0459	0.0230	0.0153	0.0115	0.0092	0.0061	0.0046	0.0023
Values using average crustal F and Gd								
Tritium (T.U.)	0.0389	0.0195	0.0130	0.0097	0.0078	0.0052	0.0039	0.0019

TABLE 4. Reservoir data and estimated mean residence times (in years) in Valles caldera, New Mexico.

Name	Date	Depth m	Temp °C	Cl[a] mg/kg	^{3}H T.U.	PF* years	WM* years	Vol. 1[b] km^3	Vol. 2[b] km^3	ref[c]
Valles Reservoir, Redondo Creek Subsystem										
Baca 4[d]	7/2/82	>1000	297	2670	0.49	45	5400	2.74	9.56	V
Baca 13[d]	7/1/82	>1000	279	2594	0.61	41	4340	2.20	7.68	V
Baca 15[d]	7/23/82	>1000	267	3257	0.25	57	>10,000	>5.07	>17.7	V
Baca 15[d]	9/7/82	>1000	326	3302	0.18	63	>10,000	>5.07	>17.7	V
Baca 19[d]	10/15/82	>1000	223	3340	0.47	46	5630	2.85	9.97	V
Valles Reservoir, Sulphur Springs Subsystem										
Baca 3[e]	6/22/88	518	190	2010	0.63	40	3140	1.59	5.56	Me
Baca 3[d]	6/22/88	335	165	1880	0.55	43	3600	1.83	6.37	Me
VC-2A[d]	5/12/87	490	210	1545	0.72	38	2880	1.46	5.10	Mu
VC-2A[d]	5/13/87	490	210	1400	0.64	40	3250	1.65	5.75	Mu
VC-2A[f]	5/14/87	490	210	2180	0.61	41	3410	1.73	6.04	Mu
VC-2A[d]	7/30/87	490	210	2620	0.47	46	4430	2.25	7.84	Mu
VC-2A[d,h]	8/27/87	490	210	2945	0.06(?)	82	>10,000	>5.07	>17.7	Mu
VC-2A[d]	12/2/87	490	207	2250	0.75	37	2770	1.40	4.90	S
VC-2B[g]	6/21/89	1753	295	0.63	0.67	39	2800	1.42	4.96	S
VC-2B[j,k]	10/26/89	1753	295	6990	0.77	37	2440	1.24	4.32	S
VC-2B[j,k]	1/18/90	1753	295	8380	0.89	37	2000	1.01	3.54	S
VC-2B[f]	6/15/91	640-1457	225	3907	0.45	46	3790	1.92	6.71	S
VC-2B[d]	6/16/91	640-1457	225	2670	0.11	71	>10,000	>5.07	>17.7	S
VC-2B[g]	6/16/91	640-1457	225	6.58	0.41	48	4160	2.11	7.36	S
VC-2B[f]	6/17/91	640-1457	225	3528	0.58	42	2940	1.49	5.20	S
VC-2B[i]	6/18/91	640-1457	225	3713	0.43	47	3970	2.01	7.03	S
VC-2B[f]	6/18/91	640-1457	225	4021	0.39	49	4380	2.22	7.75	S
VC-2B[l]	5/11/92	640-1457	225	3245	0.20	61	8140	4.13	14.4	S
VC-2B[m]	5/11/92	640-1457	225	4000	0.46	46	3530	1.79	6.24	S
VC-2B[n]	5/12/92	640-1457	225	5290	0.98	39	1640	0.83	2.90	S
VC-2B[o]	5/12/92	640-1457	225	3325	0.35	51	4640	2.35	8.21	S
VC-2B[p]	5/12/92	640-1457	225	4050	0.74	39	2180	1.11	3.86	S

* PF are piston flow model results, and WM are well-mixed model results.

a Cl values for well samples are corrected for steam flash unless otherwise noted.

b Volume 1 is calculated using the well mixed (WM) age and a minimum discharge rate of 5.07×10^{-4} km^3/yr, and Volume 2 is calculated using the well mixed age and the maximum discharge rate of 1.77×10^{-3} km^3/yr.

c V = Vuataz and Goff (1986); Me = Meeker et al., (1990); Mu = Musgrave et al., (1988); S = Shevenell and Goff (1995).

d Mini-separator sample (water).

e Bailer sample, Cl value is not flash corrected.

f Weir sample.

g Mini-separator sample (steam).

h Cl calculated from average of five flash corrected analyses (Goff, et al., 1989).

i Total flow on surface sample port.

j In-situ sample collected with down-hole sampler.

k Based on the stable isotope data, these samples appear evaporated (≤50%).

l First mini-separator sample (water); temperature = 175°C; Cl not corrected for flash.

m Second mini-separator sample (water); temperature = 144°C; Cl not corrected for flash.

n Weir box sample; temperature = 95°C.

o First mini-separator sample (water); temperature = 160°C; Cl not corrected for flash.

p Total flow from well.

recharged since atmospheric nuclear testing began has not yet reached the depths of the reservoir. If all post-bomb recharge had reached the reservoir and mixed with fluids within the reservoir, the required rate of vertical circulation would be quite high for welded, silicified tuff (6.6 m/d, assuming up to 2400 m for a circulation depth within one year). Also, due to the sluggish nature of the flow system and current views on the magnitude of dispersion, it is unlikely that the reservoir is strictly well-mixed. Hence, estimated mean residence times using the current model are likely to be too high.

Another simple mixing model can be used to demonstrate that calculated ages are likely too high, and it is unlikely that all post-bomb recharge has entered the reservoir. If we assume a constant input of 6 T.U. into the reservoir each year prior to 1953, and that this 6 T.U. decays in one year (t=1) at a rate of

$$C_{\text{year-end}} = C_{\text{begin}}\, e^{-\lambda t}, \quad (5)$$

then a simple mixing model can be used to estimate ^{3}H contents in the reservoir. This simple model assumes that the fraction of water in the reservoir (X) at initial ^{3}H content of 6 T.U. (which decays to 5.67 T.U. in one year) mixes with the fraction of water being recharged (1-X) to form the new ^{3}H content of the second year:

$$^3H_{n+1} = X(^3H_n) + (1\text{-}X)(^3H_{Rn+1}) \quad (6)$$

In this expression, $^3H_{n+1}$ is the ^{3}H content in the reservoir in year n+1 after water is recharged and mixed with existing reservoir water in year n+1. The term (^3H_n) represents the ^{3}H content in the reservoir decayed during one year before the input of recharge in year n+1 ($^3H_{Rn+1}$). After fractions of these two waters are mixed, they are allowed to decay for one year, and then the decayed mixture becomes the new ^3H_n content of the reservoir. For all years prior to 1953, $^3H_{Rn+1} = 6.0$ T.U.

The fraction of water (1-X) added to the reservoir each year (Table 5) is an obvious controlling factor in the final ^{3}H content. In all hypothetical cases, ^{3}H in the reservoir stabilizes rather rapidly (≤140 yrs) to a constant ^{3}H value through time, assuming no input of post-bomb ^{3}H. If discharge from the system is 5.07×10^{-4} km^3/yr to 1.77×10^{-3} km^3/yr, and the reservoir volume is 1.21 to 2.69 km^3 (Faust et al., 1984; Balleau, 1980; Bodvarsson et al., 1982; Union Oil, 1978, 1982), and these values are constant through time, then the fraction recharged to the system each year can be estimated. Assuming recharge equals discharge, the fraction of water entering the reservoir from one year's recharge ranges from 0.02% to 0.15% (average = 0.07%) based on these values. Hence, in the Valles reservoir, it is likely that the ^{3}H content of the water was near 0.07 T.U. prior to 1953, and that it only required 137 years (Table 5) for the content to stabilize at this value. However, it is unknown what the mean residence time of the fluids was prior to 1953, because, after 137 years, the ^{3}H content would not change with additional input. Because values in the Valles caldera are >0.07 T.U., but are as low as 0.11 T.U. in some cases, some post-bomb ^{3}H must have entered the Valles caldera system.

To estimate how many years of post-bomb ^{3}H may have entered the reservoir, equations 5 and 6 are used, substituting input ^{3}H contents from Table 1 as the recharge component for years after 1952. Table 6 lists

TABLE 5. Concentrations at which tritium stabilizes in the reservoir in the given number of years for various fractions of addition of recharge water with a tritium content of 6 T.U.

% New Water Recharged	% Reservoir Water	Final Tritium (T.U.) in Reservoir	Years to Attain Stable Tritium
0.001%	99.999%	0	133
0.07%	99.93%	0.07	137
0.10%	99.90%	0.1	140
0.50%	99.50%	0.48	120
1.00%	99.00%	0.89	109
5.00%	95.00%	2.79	89

TABLE 6. Average measured tritium and the calculated tritium contents assuming post-bomb input was contributed to the system through the years 1959, 1962, 1963, 1964 or 1966.

Sample Year	Average Tritium	Calculated Tritium with Input Through Year 1959	1962	1963	1964	1965	1966	Recharge Time (yrs)
Redondo Creek subsystem*								
1982	0.520		**0.36**	0.79				20
1982	0.215	**0.22**						23
Sulphur Springs subsystem								
1987	0.638			**0.6**	0.91			24
1988	0.590			**0.57**	0.86			25
1989	0.720			**0.54**	0.81			25.5
1990	0.890					0.85	**0.9**	24
1991	0.395		0.22	0.48				28.5
1992	0.546			**0.45**	0.69			28.5

Note: Numbers in bold show the most likely year which was the last one for which tritium entered the reservoir based on samples collected in the noted years.

* The first entry for 1982 is for Baca 4, 13, and 19, whereas the second is for Baca 15.

average ^{3}H measured in particular years in the subsystems. Equations 5 and 6 are used iteratively to calculate ^{3}H contents in a well mixed reservoir assuming no ^{3}H input to the system occurred after the particular years noted in Table 6. After the years noted, the ^{3}H in the reservoir was allowed to decay, with no further atmospheric input. By matching these calculated numbers with measured values, an estimate of the year can be made for which the last atmospheric ^{3}H entered the reservoir. The best match for part of the Redondo Creek subsystem indicates post-bomb ^{3}H was added through 1962, suggesting a 20 yr lag time between precipitation and mixing with the reservoir (recharge time). The Baca 15 well apparently taps older water and the calculations suggest that no post-1959 precipitation had reached the reservoir by the sampling date in 1982 (23 yr lag), under the current assumptions. The best match for most of the Sulphur Springs subsystem samples suggests post-bomb ^{3}H was added through 1963, with a lag time between precipitation and mixing with the reservoir of 24 to 28.5 yrs (average 25.9 yrs). Hence, recharge waters may take slightly longer to mix with reservoir waters in the Sulphur Springs subsystem than in the Redondo Creek area.

The well-mixed ^{3}H Fortran model (Shevenell and Goff, 1995) was then rerun using input ^{3}H through the years highlighted in bold on Table 6 for the particular year of sampling. For instance, recharge is assumed to have reached the reservoir in 1963 for samples collected in 1987, 1988, 1989, 1991 and 1992 in the Sulphur Springs subsystem. Because much less ^{3}H is input to the system if input is ceased at 1963, rather than in the year the sample was collected, calculated mean residence times are much lower. Table 7 shows the original estimates and the calculated mean residence times assuming no further input had reached the reservoir after the years noted in Table 6. There is much less distinction in ages between the two subsystems when it is assumed that some post-bomb ^{3}H has not entered the reservoir. There are younger waters (660 - 975 yrs) and older waters (1060 - 1270 yrs) in both subsystems, and these values are similar to those obtained using the estimated volume divided by the estimated discharge rate (1900 years; Faust et al., 1984; Balleau, 1980; Bodvarsson et al., 1982; Union Oil, 1978, 1982). The original estimates made with the assumption that all post-bomb ^{3}H was recharged and mixed in the reservoir are clearly overestimates. However, the second, lower estimates are also subject to some uncertainties. For instance, a 0.07% input to the system through recharge on a yearly basis was used to infer that no post-1959, 1962, 1963 or 1966 water entered the reservoir. The percent of recharge waters on average could be greater or less then this assumed value, and variations in this value would result in changes in the year found to be the final one in which the reservoir received recharge. Also, this percentage value may change year to year as some years may experience more precipitation than other years. Thus, in some years, high ^{3}H could have entered the reservoir in larger volumes if precipitation was abnormally high in those years, resulting in higher ^{3}H input to the system than is estimated assuming a constant input (or vice versa). In addition, pumping tests were conducted at the various wells at different times. The cone of depression could have pulled younger waters from shallower depths toward these wells, at least for the short period of time of the tests. Hence, the mean residence time estimates could be higher or lower depending on the interplay between these factors, but in general terms, the results suggest that residence times are on the order of 1000 years. If more ^{3}H was added to the system after 1963, when values in precipitation were very high (Table 1), then actual residence times could be much greater than 1000 years, and approach the values obtained in the well-mixed model (Shevenell and Goff, 1995), assuming all precipitation up to the date of sample collection had mixed with the reservoir.

TABLE 7. Estimated mean residence time of Valles caldera fluids assuming all water precipitated until the date of sample collection mixes with fluid in the reservoir ('Collection Year' column), and assuming only some post-bomb tritium recharges the reservoir ('1962, 63 or 1966' column).

	# of Samples	Ave. Tritium (T.U.)	Std. Dev.	Collection Year	Ave. Residence Time for Input Through Collection Year	Std. Dev.	"1962, 63" or 1966	Std. Dev.
Redondo Creek Subsystem								
Baca 4, 13, 19	3	0.520	0.076	1982	5123	688	789	111
Baca 15	2	0.215	0.049	1982	>10,000		1279	300
Sulphur Creek Subsystem								
VC-2A	5	0.628	0.011	1987	3348	659	870	175
Baca 3	2	0.590	0.056	1988	3370	325	869	86
VC-2B	2	0.720	0.070	1989	2620	255	666	68
VC-2B	1	0.890		1990	2000		1270	
VC-2B	5	0.452	0.075	1991	3848	553	974	144
VC-2B	5	0.546	0.313	1992	4026	2581	1013	666

The mean residence times of the two subsystems of the reservoir are somewhat different based on the older age estimates (Table 4). This is reasonable because waters in each subsystem have different flow paths and evolutions. Based on Sr isotope data, the waters in the Sulphur Springs subsystem circulate mainly in the Precambrian and Paleozoic rocks, whereas those in the Redondo Creek subsystem are generally restricted to the Quaternary caldera fill rocks (Goff et al., 1992). Permeabilities in these units are expected to differ, hence, different travel times in the respective reservoirs should also differ, and this is borne out by the maximum mean residence times. In addition, the Sulphur Springs subsystem occupies a smaller area than does the Redondo Creek subsystem. Hence, the smaller fluid volumes estimated for the Sulphur Creek subsystem are reasonable (Table 4; Shevenell and Goff, 1995). The younger age estimates (Table 7) suggest less distinction between the two subsystems. It is likely that some post-bomb ^{3}H has not entered the reservoir, but the scenario presented here is only one possibility. If the 1987 samples do indeed contain some ^{3}H through 1963, then the 1988 samples should contain some 1964 waters. The scenario presented here merely serves as one of many examples which could be conceived. If actual, yearly recharge amounts and variations by year were known and used in the calculations, more accurate estimates could be made and differences in mean residence times between the two subsystems would likely become more apparent.

CONCLUSIONS

Tritium was used to define upper limits on mean residence times of fluids within the Valles caldera reservoir using the well-mixed end-member model, and maximum values range from 3000 to 10,000 years. Although these values overestimate the residence times in the reservoir, this information required fewer data and less modeling time than the more rigorous, numerical models which need data input for numerous parameters such as the spacial variability in porosities, hydraulic conductivities, and dispersivities. The only requirement for use of the well-mixed model here is measured ^{3}H of the reservoir waters and information on post-bomb ^{3}H contents in precipitation, which is readily available at many localities. Even though measured ^{3}H contents are low in the reservoir waters, in situ production of ^{3}H in the reservoir is very low (0.01 T.U.) and insufficient to change the estimated mean residence times at Valles caldera. When taking into consideration the likelihood that not all post-bomb ^{3}H has entered the reservoir, considerably younger residence times are obtained suggesting that reservoir fluids may have a residence time a low as 1000 yrs.

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